

The Combining Weight of Gelatin as an Acid

The Mobility of the Gelatinate Ion

The Transference Numbers and Activities
of Sodium Hydroxide in Aqueous Solution

A DISSERTATION

Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the University of Michigan

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THE COMBINING WEIGHT OF GELATIN AS AN ACID

BY A. L. FERGUSON AND A. W. SCHLUCHTER*

(From the Chemical Laboratory of the University of Michigan, Ann Arbor)

(Accepted for publication, January 5, 1932)

The nature of the reactions between proteins and electrolytes has occupied the attention of many investigators. The majority support the theory that proteins when pure are definite chemical compounds and that they react with electrolytes to form highly ionizable salts. There are, however, many who choose to explain all such reactions on the basis of adsorption. This question has been extensively studied by Schmidt and his coworkers, by Cohn, and by several at The Rockefeller Institute, particularly Loeb, Hitchcock, Northrop, and Simms. Good brief summaries of the work along this line are contained in recent articles by Rawlins and Schmidt,¹ Cohn,² and Stearn.³ The authors feel, therefore, that it is not necessary to discuss the present status of the problem here.

In previous publications⁴⁻⁶ one of the authors has described work in which a study was made of the nature of the reaction of gelatin in acid solutions. The combining weight of dry gelatin in hydrochloric acid was found to be 1090 gm.

The present work is a study of the reaction of gelatin in alkaline solutions. Cells of the following types were used:

$\text{H}_2/\text{NaOH } C/\text{KCl (sat.)}/\text{NaOH } C + \text{gelatin } x \text{ gm.}/\text{H}_2$ I

$\text{Na}_y \text{ Hg}/\text{NaOH } C/\text{KCl (sat.)}/\text{NaOH } C + \text{gelatin } x \text{ gm.}/\text{Na}_y \text{ Hg}$ II

* Rewritten from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Michigan.

¹ Rawlins, L. M. C., and Schmidt, C. L. A., *J. Biol. Chem.*, 1930, **88**, 271.

² Cohn, E. J., *J. Phys. Rev.*, 1925, **5**, 349.

³ Stearn, A. E., *J. Gen. Physiol.*, 1928, **11**, 377.

⁴ Ferguson, A. L., and France, W. G., *J. Am. Chem. Soc.*, 1921, **43**, 2161.

⁵ Ferguson, A. L., and Bacon, E. K., *J. Am. Chem. Soc.*, 1927, **49**, 1921.

⁶ Ferguson, A. L., and Bacon, E. K., *J. Am. Chem. Soc.*, 1927, **49**, 1934.

Liquid junction potential was reduced to a minimum by means of saturated KCl. From Type I cells was determined the change in hydroxide ion activity produced by definite quantities of gelatin. In a similar manner, the change in sodium ion activity was obtained from the Type II cells.

Materials and Apparatus

The NaOH used was prepared from sodium amalgam and distilled water which had been boiled *in vacuo*. To prepare the amalgam, mercury was covered with several inches of kerosene and sodium added in about 5 gm. lots. The amalgam was separated by means of a separatory funnel and carefully washed with distilled water. The reaction between amalgam and water was aided by a nickel cathode which dipped into the water. The cathode was short-circuited through an ammeter to the amalgam. Sodium hydroxide so formed did not give a test for either potassium or carbonate.

The gelatin used was a special ash-free material obtained from the Eastman Laboratory. It contained 12 per cent moisture.

The hydrogen electrodes were made from platinum foil about 1 cm. square. They were platinized in the usual manner. At least two electrodes were used in each chamber. It is reported in the literature that hydrogen electrodes cannot be used satisfactorily in gelatin solutions, and it was found in this work that after continued use there was evidence of contamination; but the difficulty was easily removed by treating the electrodes with fuming nitric acid and then using them as cathode in the electrolysis of a dilute NaOH solution. After such treatment the electrodes invariably checked to within less than 0.03 mv.

Amalgam electrodes have been described by many authors. It was found that the presence of gelatin in the solution rendered the potential of these electrodes less constant so that reliable measurements could not be taken in the more dilute NaOH solutions nor in solutions containing much gelatin.

The measuring apparatus included a Type K potentiometer and necessary accessories. The standard cell was calibrated by the Bureau of Standards. The temperature was regulated at $25^{\circ}\text{C.} \pm 0.01$.

Cells Used and Experimental Procedure

The cell assembly for Type I is represented in Fig. 1. Flasks of about one liter capacity were provided with five necks to accommodate hydrogen electrodes, gas inlet, and outlet, etc. Flask *A* contained pure NaOH solution; *A'* contained NaOH of the same concentration as *A* but in addition a known weight of gelatin.

A uniform method of procedure was adopted in making the gelatin NaOH solutions. The desired weight of gelatin was placed in a beaker and an amount of distilled water sufficient to dissolve it added. The water was kept at about 35°C. and frequently stirred. This solution was then transferred to a calibrated

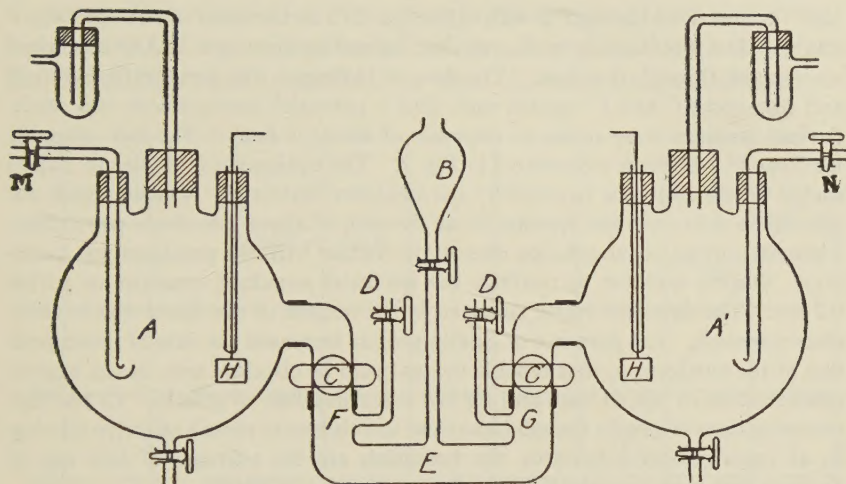


FIG. 1. The cell assembly for systems of the type
 $\text{H}_2/\text{NaOH } C//\text{NaOH } C + x \text{ gm. gelatin}/\text{H}_2$

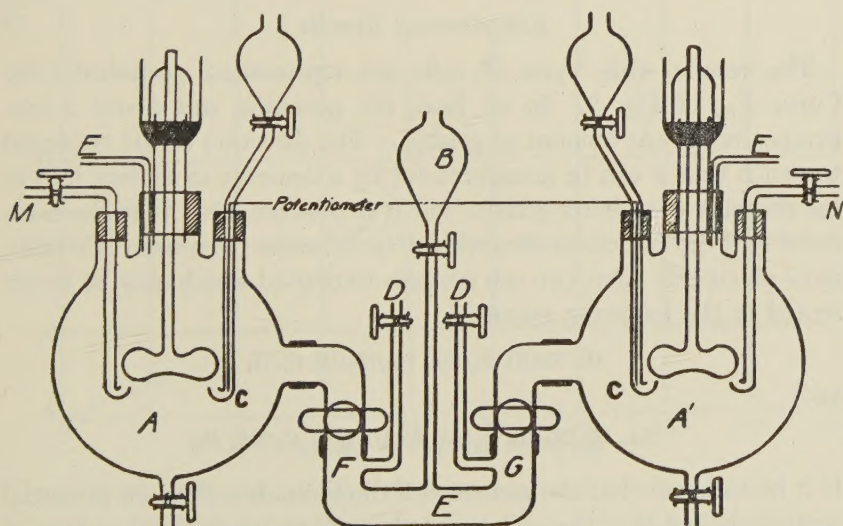


FIG. 2. The cell assembly for systems of the type
 $\text{Na}_2\text{Hg}/\text{NaOH } C//\text{NaOH } C + x \text{ gm. gelatin}/\text{Na}_2\text{Hg}$

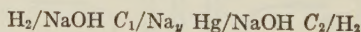
liter flask. The amount of NaOH of known concentration required to give the desired concentration was added and the whole diluted to 1 liter. The intermediate vessel was designed to reduce so far as possible the liquid junction poten-

tial. It was filled through *B* with saturated KCl to the level of the openings *F* and *G*. The junction, say at *F*, was then formed by opening *C*. Any entrapped air escaped through the flask. The flow of hydrogen was temporarily shut off and stop-cocks *C* and *C'* opened each time a potential measurement was made. Several readings were taken at intervals of about 1 hour. The cell assembly for Type II systems is represented in Fig. 2. The equipment is similar to Type I except for the additions required by the amalgam electrodes. The amalgam was allowed to drip from the openings *C* at the rate of about two drops per second. Vigorous stirring of the solution directly in contact with the amalgam was necessary. During each set of readings the potential remained constant to within 0.2 mv. The amalgam which collected in the bottom of the flasks was immediately removed. The presence of gelatin greatly increased the rate of decomposition of the amalgam so that reliable values could be obtained only in the highest concentration of NaOH used and for low concentrations of gelatin. In the high concentrations of gelatin the solutions were too viscous to permit effective stirring. In all cases recorded, however, the potentials are the averages of four sets of readings and were reproducible to a few tenths of a millivolt.

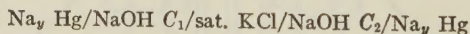
It was found necessary to protect all glass which would otherwise come in contact with NaOH solution by a coating of paraffin.

Experimental Results

The results with Type II cells are represented graphically by Curve E_{Na} of Fig. 5. In all cases the potential was about 2 mv. irrespective of the amount of gelatin. The direction of the potential was such that it can be accounted for by a decrease in sodium ions in the chamber containing gelatin; but it is possible, also, that the saturated KCl did not eliminate completely diffusion potential. To learn more about this point two cell systems were used which may be represented in the following manner:



and



If it be assumed that the saturated KCl eliminates diffusion potential completely and that the activity of the sodium ion is equal to that of the hydroxide ion in NaOH of a given concentration, then the potential of the first system should be just double that of the second. The latter assumption is probably true at the concentration used.⁷ When

⁷ Lewis, G. N., and Randall, M., *Thermodynamics*, New York, McGraw-Hill Book Co., Inc., 1923, 381.

C_1 was 0.0033 N and C_2 0.1 N, the discrepancy in values was found to be about 2.4 mv. For smaller differences in NaOH concentrations the potentials would probably be less. It may be assumed, there-

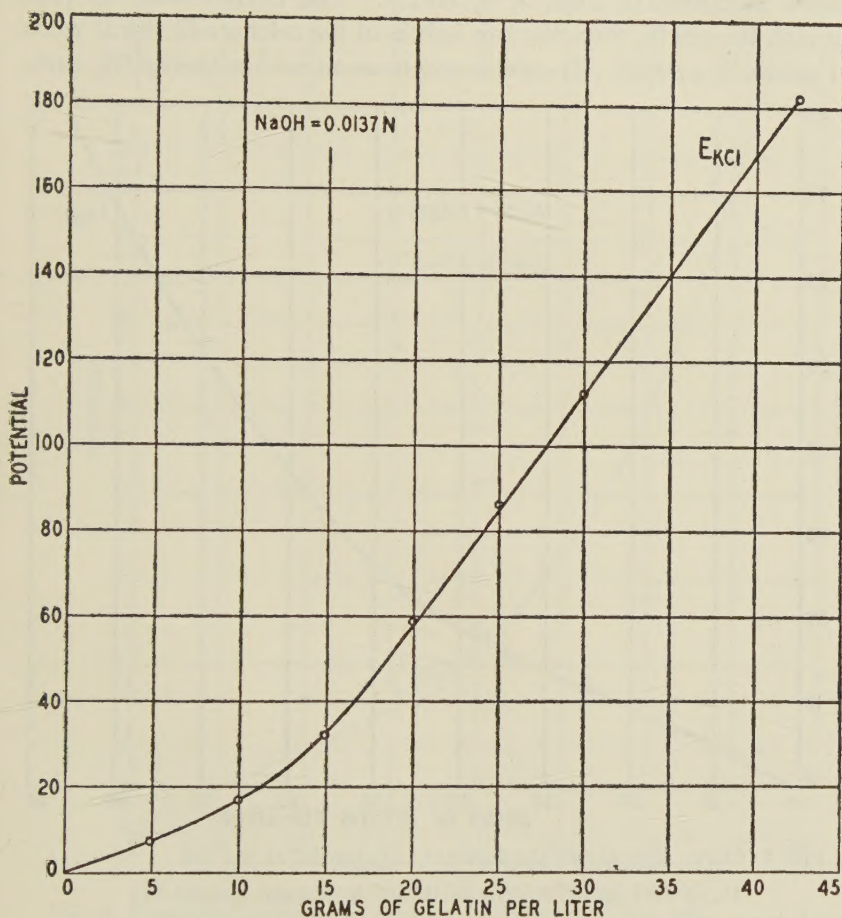


FIG. 3. Curve E_{KCl} shows the increase in potential of the cell $H_2/NaOH$ 0.0137 N//NaOH 0.0137 N + x gm. gelatin/ H_2 as x is increased.

fore, that the E_{Na} potentials for System II were due to uneliminated junction potentials. It is safe to conclude that the change in sodium ion concentration produced by the action of gelatin upon NaOH is

less than that represented by a potential of 2 mv. and is probably entirely insignificant.

Three concentrations of NaOH were used and the data are represented as curves in Figs. 3, 4, and 5. The curves must all pass through the origin, since the two halves of the cells are identical when no gelatin is present. If gelatin reacts as an acid with NaOH, then,

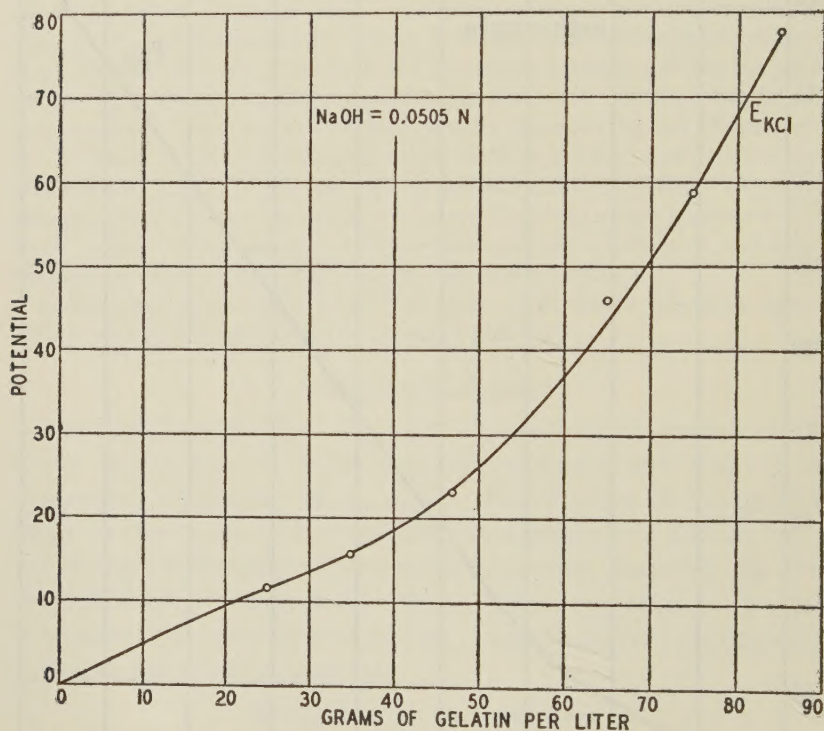


FIG. 4. Curve E_{KCl} shows the increase in potential of the cell $H_2/NaOH\ 0.0505\ N/NaOH\ 0.0505\ N + x\ gm.\ gelatin/H_2$ as x is increased.

in the chamber containing gelatin, the hydroxide and thus the hydrogen ion concentration is changed. The potentials represented by the curves are due only to changes in hydrogen ion concentration produced in this manner. The potentials should be given by the formula

$$E_{KCl} = \frac{RT}{NF} \ln \frac{a'_H}{a''_H} = \frac{RT}{NF} \ln \frac{a''_{OH}}{a'_{OH}} = \frac{RT}{NF} \ln \frac{C''_{OH} \gamma''}{C'_{OH} \gamma'}$$

where the activity, concentration, and activity coefficient of the OH ions in the pure NaOH solution are represented respectively by

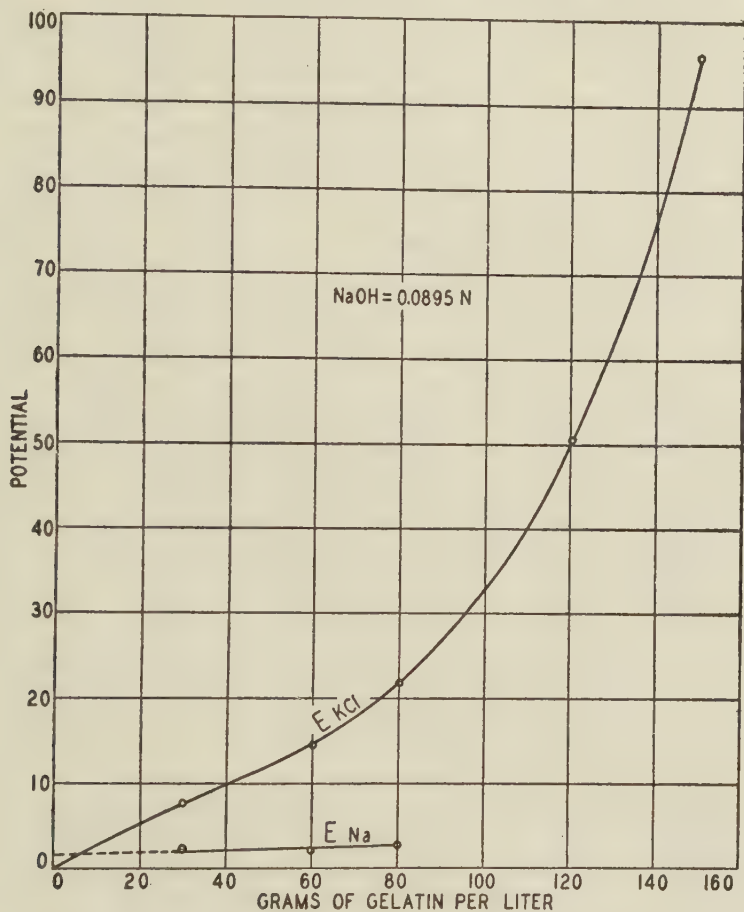


FIG. 5. Curve E_{KCl} shows the increase in potential of the cell

$H_2 \cdot NaOH \text{ } 0.0895 \text{ N} // NaOH \text{ } 0.0895 \text{ N} + x \text{ gm. gelatin} / H_2$

as x is increased.

Curve E_{Na} shows the increase in potential of the cell

$Na_v Hg / NaOH \text{ } 0.0895 \text{ N} // NaOH \text{ } 0.0895 \text{ N} + x \text{ gm. gelatin} / Hg Na_v$

as x is increased.

a''_{OH} , C''_{OH} , and γ'' ; and in the solution which originally had the same OH ions activity, but to which known quantities of gelatin were

added, the resulting activity, concentration, and activity coefficient of OH ions are represented by a'_{OH} , C'_{OH} , and γ' .

It was pointed out above that the potentials with sodium amalgam electrodes showed the sodium ion activity to be unchanged by the addition of gelatin. This means that the sodium gelatinate formed is highly dissociated. It is not unreasonable to assume therefore that the activity coefficient of the OH ions remains unchanged as gelatin is added to the NaOH. Cohn has shown that this is the case when NaOH is neutralized by four acids,—sulfuric, oxalic, glutamic and aspartic. If this is true then $\gamma' = \gamma''$ and the actual concentration of NaOH remaining unneutralized after each addition of gelatin is given directly from the potential measurements and the above formula.

This is practically the same method as introduced by Bugarsky and Liebermann⁸ and later used by Robertson.⁹ Another method introduced by Tague¹⁰ and adopted by several involves the measurement of a "blank," *i.e.*, the amount of reagent required to change the water to the same pH as the solution under consideration. As Tague pointed out, it is not necessary to take into account the degree of ionization by this method. It must be remembered, however, that the hydrogen electrode measures activity, and in the "blank" employed there is nothing present but NaOH, while in the neutralized system there is ionized salt in addition. In calculation, therefore, it must be assumed that the ionized salt has no influence upon the activity of the hydroxide ions. This source of error has been pointed out by Cohn and Berggren.¹¹

In the determination of base combining power of proteins, Cohn and Berggren measured the potential of the hydrogen electrode in the solution containing base and protein against a 0.1 N calomel electrode. They also measured or calculated the pH of the pure NaOH solutions. The pH was calculated by the equation

$$\text{pH} = \frac{\text{E.M.F. observed} - \text{E.M.F. 0.1 N calomel}}{0.001983 T}$$

⁸ Liebermann, L., *Arch. ges. Physiol.*, 1898, **72**, 51.

⁹ Robertson, T. B., *The physical chemistry of the proteins*, New York, London, Bombay, Calcutta, and Madras, Longmans Green and Co., 1918.

¹⁰ Tague, E. L., *J. Am. Chem. Soc.*, 1920, **42**, 173.

¹¹ Cohn, E. J., and Berggren, R. E. L., *J. Gen. Physiol.*, 1924-25, **7**, 45.

From this they obtained p_{OH} from the relation

$$p\text{H} + p_{\text{OH}} = pK_{\text{W}}$$

and ultimately the stoichiometric concentration by the equation

$$(\text{NaOH}) = \frac{(\text{OH})}{\gamma}$$

The activity coefficient is thus involved in all of their calculations of bound NaOH. This would not have been necessary, however, if they actually measured the pH of each of the pure NaOH solutions used and had assumed that the activity coefficient of the hydroxide ions remained constant. In some cases they made such measurements and attempted to show that different values for the base binding power of casein are obtained according to whether Robertson's or their method of calculation is used. If no errors are involved in the potential measurements due to a lack of elimination of boundary potential in the one case and the assumption that the boundary potential between the calomel electrode and each of the other solutions is zero or the same for both in the other case, then the two methods must give the same value since the activity coefficient does not enter into the calculation in either case and the same formula is used.

The combining weights obtained for various quantities of gelatin are recorded in Table I. The first value for each concentration is not included in the averages, since the per cent error in the measurements for these values is much greater than for the others.

Combining weights were not calculated for the larger amounts of gelatin, because these are greater than that required for complete combination. The quantities of gelatin for complete combination are 21.3 gm. for the 0.0137 N NaOH, 78.6 gm. for the 0.0505 N, and 139 gm. for the 0.0895 N.

It should be observed: first, that the combining weight of gelatin obtained here is independent of the concentration of NaOH; second, that in each of the three concentrations of NaOH the combining weight of gelatin is independent of the ratio of base to gelatin. In other words, the combining weight of gelatin remains practically constant through a wide pH range. These facts cannot be accounted for on the basis of adsorption.

For quantities of gelatin near the end-point the amount of NaOH that remains is too small to prevent hydrolysis and the method does not apply. In fact the last combining weight value recorded for 0.0137 N is higher than all others obtained and this is due probably to hydrolysis.

Various values for the combining weight of gelatin as an acid are recorded in the literature. The values appear to depend upon both the method used and the investigator.

In his extensive and highly valuable review of the physical chemistry of the proteins, Cohn¹² states, "A recalculation of Loeb's¹³ and Hitch-

TABLE I
Combining Weights of Gelatin (not Corrected for Moisture)

Conc. of NaOH 0.0137 N		Conc. of NaOH 0.0505 N		Conc. of NaOH 0.0895 N	
Gelatin per liter	Combining weight	Gelatin per liter	Combining weight	Gelatin per liter	Combining weight
<i>gm.</i>		<i>gm.</i>		<i>gm.</i>	
5	1430*	25	1360*	30	1310*
10	1475	35	1530	60	1570
15	1520	47	1560	80	1570
20	1620	65	1555	120	1570
25		75		150	
30		85			
42.5					
Average . . .	1538		1548		1570

* These values were not included in averages.

cock's¹⁴ electromotive force measurements yield 56, 57, and 56×10^{-5} mols per gram as the combining capacity. Greenberg and Schmidt¹⁵ report an almost identical value of 60×10^{-5} mols per gram, and this is the highest base combining capacity that Atkin and Douglas¹⁶ measurements reveal upon recalculation."

¹² Cohn, E. J., *Physiol. Rev.*, 1925, 5, 349.

¹³ Loeb, J., *J. Gen. Physiol.*, 1920, 3, 85.

¹⁴ Hitchcock, D. I., *J. Gen. Physiol.*, 1923, 6, 457.

¹⁵ Greenberg, D. M., and Schmidt, C. L. A., *Proc. Soc. Exp. Biol. and Med.*, 1924, 21, 281.

¹⁶ Atkin, W. R., and Douglas, G. W., *J. Soc. Leather Trades' Chemists*, 1924, 8, 584.

Loeb, in the article referred to, makes no attempt to calculate the combining weight; in fact the data given would have to be corrected for the amount of base required to give the water alone the respective pH values. The same statements apply also to the data of Hitchcock to which reference is made.

Concerning the data of Atkin and Douglas, Miss Lloyd in her book, *Chemistry of the proteins*, published in 1926, makes the statement that their data show "combination of gelatin and bases takes place in two stages, the first in which 1 gm. combines with about 30×10^{-5} equivalents of base, the second in which 1 gm. combines with 80×10^{-5} equivalents." In another place, however, Miss Lloyd states, "Atkin and Douglas find 30×10^{-5} for a first stage of titration and 70×10^{-5} for a second stage." This discrepancy in statements is easily understandable since the pH combination curve shows no sharp break and it is largely a matter of choice whether to take 70×10^{-5} which is the value for pH 11 or 80×10^{-5} which is the value for pH about 13. I do not, however, understand how Cohn gets the low value 60×10^{-5} from their data as "The highest base combining capacity that Atkin and Douglas' measurements reveal upon recalculation."

In the article by Greenberg and Schmidt, referred to by Cohn, they estimate the base combining capacity of gelatin upon the recent analysis of gelatin by Dakin.¹⁷ He reports the base binding power of the aspartic acid present in gelatin to be 26×10^{-5} and of glutamic acid to be 39×10^{-5} or a total of 65×10^{-5} . From this he subtracts 23×10^{-5} , the amide nitrogen, thus leaving a combining capacity of 42×10^{-5} . They report that the actual found binding capacity at pH 11 is 60×10^{-5} . Greenberg and Schmidt do not include their data but state, "Our method of estimating the base combining power of the proteins was carried out according to the procedure which has previously been used by Tague¹⁸ for amino acids and by Loeb and Hitchcock for proteins. On account of the logarithmic increase in pH on addition of alkali the method is not capable of a very high degree of accuracy at high alkalinity."

In view of this analysis of the literature one might question the

¹⁷ Dakin, H. D., *J. Biol. Chem.*, 1920, **44**, 499.

¹⁸ Tague, E. L., *J. Am. Chem. Soc.*, 1920, **42**, 173.

statement of Cohn, "The maximum base combining capacity of gelatin is extremely well known." Later developments render the statement even more questionable and also the combining value about 56×10^{-5} which he appears to accept. Simms¹⁹ has carried out what appears to be a highly accurate electrometric titration of gelatin throughout the range from about pH 1.5 to pH 11.5. He indicates a maximum base combining capacity of 70×10^{-5} .

The conductometric method has been applied in what appears to be a carefully performed series of experiments by Stearn.²⁰ Base is titrated with gelatin and also gelatin with base. By the former

TABLE II
Summary of Values for Equivalent Weight of Gelatin As an Acid

Author	Date	Combining weight
Loeb.....	1920	1790 recalculated by Cohn
Hitchcock.....	1923	1790 " " "
Greenberg and Schmidt.....	1924	1670
Atkin and Douglas.....	1924	1670 according to Cohn
" " "	1924	3330 (pH ₉) and 1250 (pH ₁₁) according to Lloyd or 1430 (pH ₁₃)
Estimated from acid content as determined by Dakin.....		1540 or 2380
Simms.....	1928	1430
Stearn.....	1928	1320
"	1928	1360
Rawlins and Schmidt.....	1929	1430
Ferguson, Schluchter.....	1931	1370

method he obtains for the combining capacity 75.8×10^{-5} and by the latter 73.5×10^{-5} .

Schmidt and his coworkers have studied the combining power of gelatin for acid and basic dyes. They find that the maximum combining power is found only in strongly acid or basic solutions. Rawlins and Schmidt²¹ show that the combining power of gelatin for methylene blue, safranin γ , and induline scarlet is approximately the same. They give for pH 11 a combining capacity 70×10^{-5} .

¹⁹ Simms, H. S., *J. Gen. Physiol.*, 1927-28, 11, 629.

²⁰ Stearn, A. E., *J. Gen. Physiol.*, 1928, 11, 377.

²¹ Rawlins, L. M. C., and Schmidt, C. L. A., *J. Biol. Chem.*, 1929, 82, 709.

An uncertainty that enters into many of the values given is the condition of the gelatin. It is seldom stated whether dry gelatin was used. Gelatin ordinarily contains about 10 per cent or more moisture. Stearn states specifically that his values are for dry gelatin.

The average of all the values for the combining weight obtained in the present investigation, corrected to 1 gm. of dry gelatin, is 73×10^{-5} . The gelatin used contained 12 per cent moisture.

Since this work was prepared for publication the excellent recent work of Hitchcock²² has come to the attention of the authors. The combining capacity of gelatin for NaOH is extremely indefinite according to his data, though the value 84×10^{-5} obtained with Eastman Purified Gelatin, Lot 51, is of the same order of magnitude at least as the value obtained in this work.

SUMMARY

1. The nature of the reaction between gelatin and sodium hydroxide has been studied at three concentrations of gelatin.
2. Gelatin appears to react stoichiometrically with sodium hydroxide.
3. The addition of gelatin to sodium hydroxide does not change the concentration of sodium ions in the solution.
4. A given amount of gelatin reacts with the same amount of sodium hydroxide no matter what the concentration of sodium hydroxide or ratio of sodium hydroxide to gelatin, provided there is sufficient excess of sodium hydroxide to prevent hydrolysis.
5. The combining weight of dry gelatin as an acid is found to be 1370 gm.

²² Hitchcock, D. I., *J. Gen. Physiol.*, 1931, **15**, 125.

THE MOBILITY OF THE GELATINATE ION

BY A. L. FERGUSON AND A. W. SCHLUCHTER*

(From the Chemical Laboratory of the University of Michigan, Ann Arbor)

(Accepted for publication, January 5, 1932)

Many attempts have been made to determine the mobilities of large ions or charged particles of colloidal dimensions. Several methods have been used based upon the movement of charged particles under a difference of potential. They may be grouped into three classes: (1) conductivity; (2) transport numbers, (*a*) Hittorf method, (*b*) moving boundary method, (*c*) electromotive force method; (3) cataphoresis.

From a review of the literature on this subject one is impressed by the lack of uniformity in results obtained with different methods and by different investigators.

According to the earlier generally accepted ideas concerning ion velocities it is to be expected that protein ions should have low mobilities, and some investigators have reported low values. Hardy¹ found, by the conductivity method at 18°C., about 7.5 for the mobility of the globulinate ion. The moving boundary method gave him about 9 for the globulin ion in chloride solution and about 7 for the globulinate ion in sodium globulinate.

Pauli,^{2,3} McBain,⁴ Greenberg and Schmidt,⁵ Svedberg⁶ and their coworkers all found that the mobilities of protein ions depend upon the relative amounts of the protein and acid or base in the solution. Pauli found by the conductivity method that the mobility of the protein ion increased from about 10 in a strongly alkaline solution to a constant

* Rewritten from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Michigan.

¹ Hardy, W. E., *J. Physiol.*, 1905, **33**, 251.

² Pauli, W., *Anz. Akad. wissenschaft. Wien*, 1913, No. 24.

³ Pauli, W., *Biochem. Z.*, 1919, **99**, 219.

⁴ McBain, J. W., and Salmon, C. S., *J. Am. Chem. Soc.*, 1923, **42**, 426.

⁵ Greenberg, D. M., and Schmidt, C. L. A., *J. Gen. Physiol.*, 1924-25, **7**, 287, 303.

⁶ Svedberg, T., *J. Am. Chem. Soc.*, 1924, **46**, 2700.

value of about 30 as the protein content was increased. The boundary potential method gave him, for a solution containing 1 per cent albumin in 0.002 N HCl, a mobility of 5-8.

Scott and Svedberg, by a special arrangement of the moving boundary method, were able to measure directly the velocity of protein ions. They reported a maximum mobility of about 20 in acid solution.

By the conductivity method, Greenberg and Schmidt found for the caseinate ion at 25°C. values from 25.9 to 36.2 depending upon the alkali used. They were unable to obtain results with the moving boundary. The Hittorf method gave them values from 43 to 46.5 for the caseinate ion.

The explanations for the phenomena observed fall into two general classes. According to some the colloidal particles receive their charges through hydrolysis and adsorption, while others believe they are ions which result from the dissociation of chemical compounds. For more complete discussions of this question the reader is referred particularly to the articles by Cohn,⁷ McBain and Salmon,⁴ Greenberg and Schmidt,⁵ Pauli,⁸ Robertson,⁹ and Belden.¹⁰

For the present work the authors attempted to accumulate some information concerning the migration velocity of the gelatinate ion in various relative concentrations of sodium hydroxide. It is universally accepted that a potential difference exists at the surface of contact between two solutions of electrolytes that differ in any manner whatever. Various formulas have been developed to express the magnitude of such potentials; the complexity of the formulas increases with the complexity of the system. All such formulas are based upon the assumption that the magnitude of the potential depends upon the mobilities and concentrations of the ions in the two solutions. In systems where the boundary potential can be experimentally measured and the concentrations of all the ions and the mobilities of all but one ion are known, it is possible to calculate the mobility of that one.

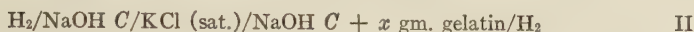
⁷ Cohn, E. J., *Physiol. Rev.*, 1925, **5**, 349.

⁸ Pauli, W., *Colloid chemistry of the proteins*, Philadelphia, P. Blakistons' Sons and Co., 1922.

⁹ Robertson, T. B., In Alexander, J., *Colloid chemistry*, New York, The Chemical Catalog Co., Inc., 1928, **2**, 255.

¹⁰ Belden, B. C., *J. Phys. Chem.*, 1931, **35**, 2164.

The two types of cells used may be represented in this manner



The same concentration of NaOH was used on the two sides of the boundary but on one side there was in addition a known quantity (x) of gelatin. The two types of cells were identical except that in II the boundary potential was eliminated by saturated KCl solution. It is evident that the difference ($E_{\text{KCl}} - E_{\text{H}}$) between the potentials of these two cells gives the boundary potential E_B .

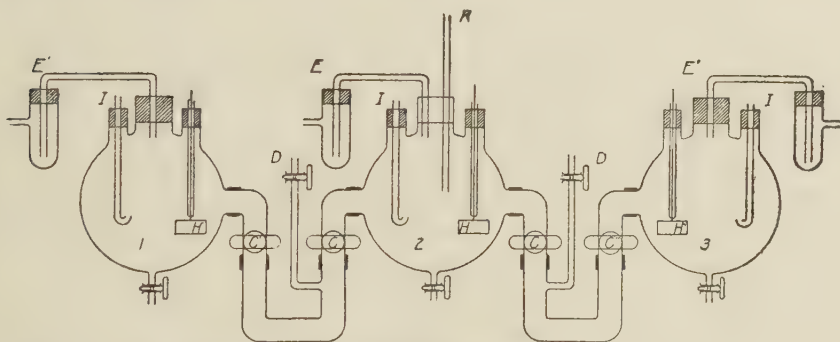


FIG. 1. The cell assembly for systems of the type



The materials used and measuring apparatus have been described in a previous paper.¹¹

The cell assembly for Type II system was the same as in Fig. 1 in the previous paper. For Type I systems the arrangement represented in Fig. 1 of this article was used. The flasks were similar to those used for Type II systems; their capacity was about 1 liter and they had five necks to accommodate the hydrogen electrodes, gas inlet, and outlet, etc. Flask 2 contained the pure NaOH solution, while Flask 1 contained NaOH of the same concentration as 1 but in addition a definite amount of gelatin. Flask 3 also contained the same concentration of NaOH but a different amount of gelatin than 1.

¹¹ Ferguson, A. L., and Schluchter, A. W., *J. Gen. Physiol.*, 1931-32, 15, 463.

This arrangement made it possible to carry on two sets of measurements at the same time. The liquid junction vessel permitted the formation of a definite horizontal boundary between the two solutions. The boundary could be renewed as frequently as desired.

To form a junction, for instance between 1 and 2, stop-cocks C' and D were opened and solution drawn out of Flask 1; C' was then closed and C opened and solution drawn out of Flask 2. The solutions in 1 and 2 were adjusted to the same level and D closed. Before taking each set of readings the hydrogen inlets were closed and stop-cocks C and C' opened. Readings were taken, (1) for boundaries that had been prepared for several minutes, (2) for freshly prepared boundaries, and (3) for flowing boundaries. The following junction was made by allowing the hydrogen to bubble slowly with C and C' open and D partly open. Potentials checked to about 0.3 mv. at the lower concentrations of gelatin, but when gelatin was present in large excess the variation reached several millivolts. Duplicate measurements were made in all cases by refilling the flasks with new solutions.

The data are represented as curves in Figs. 2 and 3. For the curves in Fig. 2 the NaOH was 0.0137 N and in Fig. 3, 0.0505 N . The data for Type I cells are represented in each figure by curves E_H , and for Type II cells by curves E_{KCl} . The E_H curves show the change in liquid junction potential with increasing amounts of gelatin, and are obtained by plotting the differences between corresponding values for E_H and E_{KCl} against grams of gelatin.

The observed data can be explained on the basis of chemical reaction between gelatin and NaOH. All curves must of course pass through the origin, since, at the start the solutions are the same in all flasks. If gelatin acts as an acid and combines with the sodium hydroxide, then the rapidly moving hydroxide ions on one side of the boundary would be replaced by heavy slow moving gelatinate ions. In a previous paper¹¹ it was shown that the activity of the sodium ion is not changed by the addition of gelatin which means that the sodium gelatinate is practically completely dissociated. The replacement of hydroxide ions by gelatinate ions is, therefore, the only change that results from the addition of gelatin and the only cause for the development of a liquid junction potential. According to this view the boundary potential should increase in value until the NaOH has been entirely

neutralized by gelatin, after which further additions of gelatin should have very little or no effect. This was found to be the situation with

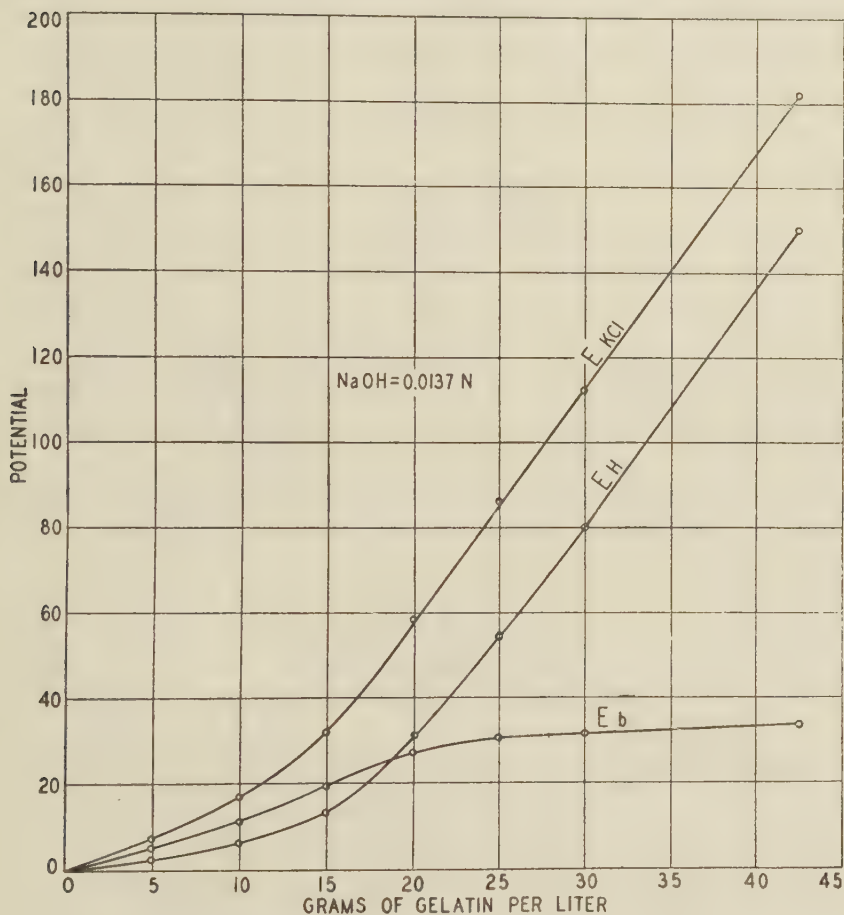


FIG. 2. Curve E_{KCl} shows the increase in potential of the cell

$H_2/NaOH$ 0.0137 N/KCl (sat.)/NaOH 0.0137 N + x gm. gelatin/ H_2 as x is increased. E_H is a similar curve for the cell

$H_2/NaOH$ 0.0137 N/NaOH 0.0137 N + x gm. gelatin/ H_2 .

Curve E_b shows the corresponding changes in boundary potential.

0.0137 N NaOH but was not strictly the case for the higher concentration. In the 0.0505 N NaOH the boundary potential reached a maxi-

mum and then dropped for the largest amount of gelatin used. This last quantity of gelatin is more than enough for complete combinations of all the NaOH, according to the combining weight reported in a previous paper. This excess gelatin may possibly explain the decrease in potential for the last point. Some recent unpublished results show

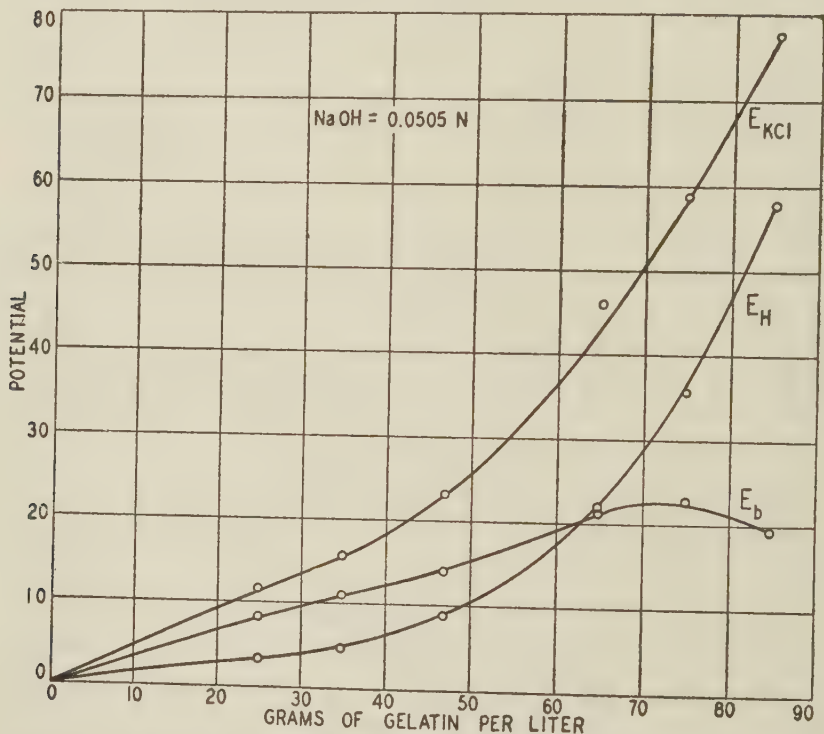


FIG. 3. Curve E_{KCl} shows the increase in potential of the cell $H_2/NaOH$ 0.0505 N/ KCl (sat.) $NaOH$ 0.0505 N + x gm. gelatin/ H_2 as x is increased. E_H is a similar curve for the cell $H_2/NaOH$ 0.0505 N/ $NaOH$ 0.0505 N + x gm. gelatin/ H_2 . Curve E_b shows the corresponding changes in boundary potential.

definitely that an excess of a very weak base in a system similar in fundamental respects to the one used in this work caused a decrease in boundary potential when the solution on the other side of the boundary was an acid. An explanation of this phenomenon will be given in a later paper.

If the assumption is correct that gelatin reacts chemically with the sodium hydroxide to form a highly dissociated salt, then the concentrations of all the ions in both solutions may be calculated from the

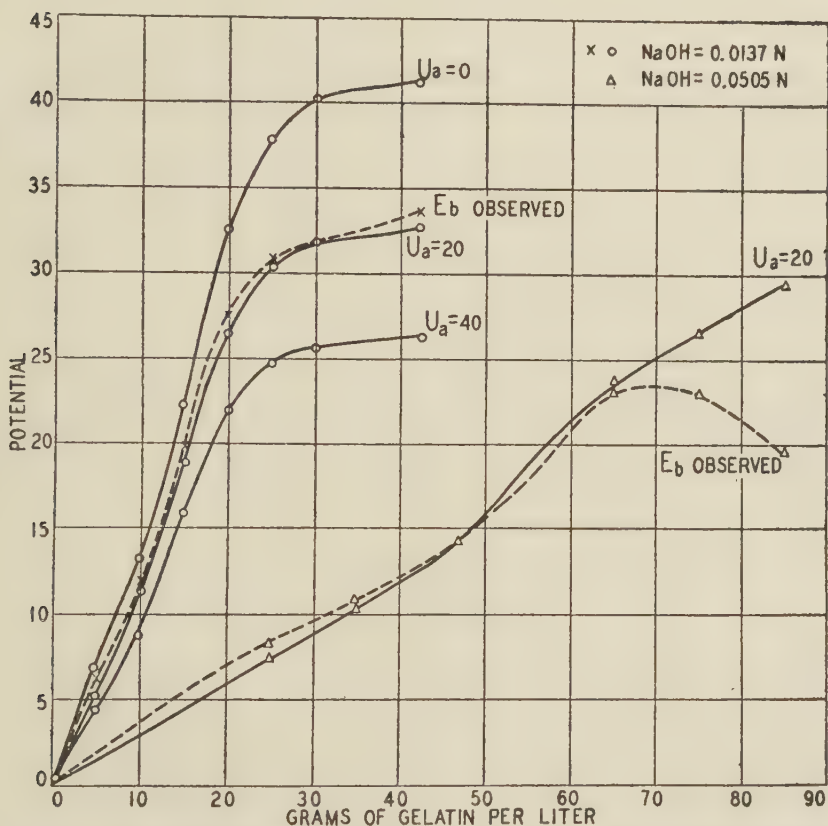


FIG. 4. Curves which represent calculated and measured values for boundary potential. $U_a = 0$, $U_a = 20$, and $U_a = 40$ represent values calculated by means of the Henderson equation and based upon the assumption of 0, 20, and 40 as the mobility of the gelatin ion. The E_b (observed) represents the measured values. The curves with circles apply to 0.0137 N NaOH and with triangles to 0.0505 N NaOH.

data obtained. The mobilities of all the ions are known except the gelatin ion. In all cases the cations are the same on both sides of the boundary and have the same concentrations, as shown in previous

work. The total anion concentrations in the two solutions is the same. For this special type of boundary the Henderson formula reduces to the form.

$$E_b = \frac{RT}{F} \ln \frac{U + V_1}{U + V_2}$$

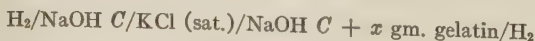
In order to calculate E_b by this formula, however, it is necessary to assume some value for the mobility of the gelatinate ion. Calculations of the potential of each boundary experimentally determined for the 0.013 N NaOH solutions were carried out with various assumed mobilities, for the gelatinate ion. The calculated values for the three assumed mobilities 0, 20, and 40 as well as the measured are represented as curves in Fig. 4.

The agreement between the observed results and those calculated on the assumption that the mobility of the gelatinate ion is 20 is striking. The differences are within the limits of experimental error. The agreement is somewhat less satisfactory for 0.0505 N NaOH solutions though it is about within the limits of experimental error except for the last two points, and an explanation has been suggested above for the low observed values.

It appears from this work that the mobility of the gelatinate ion does not depend upon the relative amounts of base and gelatin in the solution or the concentration of NaOH within the limits used. As pointed out above, others have reported a marked change in mobility with a change in relative amounts of base and gelatin. The authors suggest that possibly the difference may be due to the length of time the solutions were prepared before measurements were taken. Rawlins and Schmidt¹² have shown that days may be required to reach equilibrium in gelatin solutions. For this work the solutions were made up at 35°C., which greatly hastens equilibrium, and allowed to stand several hours and in most cases days before they were used.

SUMMARY

1. Many measurements were made with the two systems



¹² Rawlins, L. M. C., and Schmidt, C. L. A., *J. Biol. Chem.*, 1930, **88**, 271.

in which x was varied from zero to more than enough for complete combination.

2. From these measurements the change in boundary potential with quantity of gelatin present was determined.

3. The boundary potentials were calculated by means of a modified form of the Henderson equation.

4. The results indicate that the mobility of the gelatinate ion is about 20.

A paper presented at the Fifty-first General Meeting of the American Electrochemical Society, held in Philadelphia, Pa., April 30, 1927, President Blum in the Chair.

THE TRANSFERENCE NUMBERS AND ACTIVITIES OF SODIUM HYDROXIDE IN AQUEOUS SOLUTION.¹

By A. L. FERGUSON² and A. W. SCHLUCHTER.³

ABSTRACT.

The concentration cell method has been applied to the determination of the transference numbers of sodium hydroxide. The values recorded in the literature for the transference numbers of sodium hydroxide are unsatisfactory. At the same time the activity coefficients were determined up to nearly through normal concentration. The results show that the transport numbers change with concentration. N_o decreases from 0.203 at the concentration 0.01004 to 0.153 at the concentration 2.825. The activity coefficients change from 0.920 at the concentration 0.01004 through a minimum of 0.707 at the concentration 0.9738, then increase to 0.842 at the concentration 2.825.

The literature reveals no values accurately determined for the transference numbers of sodium hydroxide. The influence of concentration upon the transference numbers of sodium hydroxide has apparently received no attention. The excellent critical review by Noyes and Falk⁴ of transference number determinations mentions only two articles, the work of Bein,⁵ in which the Hittorf method was used, and the work by Dennison and Steele,⁶ who used the moving boundary method. Their values are given in Table I.

The present work is an application of the concentration cell method to the determination of the ion activities and transference

¹ Contribution from the chemical laboratory of the University of Michigan. Manuscript received February 14, 1927.

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⁴ J. Am. Chem. Soc., **33**, 1436 (1911).

⁵ Z. f. Physik. Chem., **27**, 1 (1898).

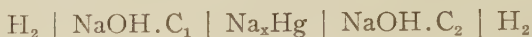
⁶ Phil. Trans., **205A**, 449 (1906).

numbers of sodium hydroxide over the concentration range 0.01 M to 3.00 M. This method has been so frequently used during the last few years that no special description need be given here.

TABLE I.

Conc.	N _c	Author	Temp. °C.
0.025-0.04 0.1	0.201 0.158	Bein Dennison and Steele	25 18

For the determination of activity coefficients the concentration double cell of the type



was used. From a combination of the potentials of cells of the above type with the potentials of cells of the type



the transference numbers were calculated.

Extensive preliminary experimenting was done with the mercury-mercury oxide electrode, but it was finally discarded as unsatisfactory. This agrees with the experiences of Knobel⁷ in his attempt to use the mercury-mercury oxide electrode in connection with his work on potassium hydroxide.

MATERIALS.

Sodium Amalgams. Amalgams were prepared by the direct combination of sodium with mercury. Reagent quality mercury was covered with about three in. (7.6 cm.) of kerosene and metallic sodium was added in five to ten-gram lots. A vigorous amalgamation took place, and the kerosene prevented the sodium from taking fire. In this way amalgam containing about 0.75 per cent sodium was formed. With higher percentages of sodium a solid or semi-solid mass resulted, which was difficult to handle. The amalgam was separated from the kerosene and carefully washed several times with distilled water, then dried. This amalgam served as stock from which both the amalgam electrodes and the sodium hydroxide solutions were made.

⁷ J. Am. Chem. Soc., 45, 77 (1923).

Sodium Hydroxide Solutions. In the preparation of sodium hydroxide solutions, the amalgam was added to distilled water, which had been freshly boiled *in vacuo*. To facilitate the decomposition the amalgam was short-circuited with a nickel electrode, which was placed in the distilled water. Sodium hydroxide solutions formed in this way gave negative tests for carbonates and potassium. All the solutions had to be stored in paraffin vessels. The various sodium hydroxide solutions used in cells were made by diluting the required amount of stock solution with distilled water, which had been freshly boiled *in vacuo*.

APPARATUS AND EXPERIMENTAL PROCEDURE.

Hydrogen Electrodes. The hydrogen electrodes were made in the usual way from platinum foil about one centimeter square. These electrodes agreed to within 0.04 millivolts in many cases for weeks. When the potential deviated more than this, the electrodes were placed in fuming nitric acid for a few seconds and then electrolyzed in dilute sodium hydroxide solution against a platinum anode. Electrodes treated in this manner invariably checked and thus eliminated frequent replatinizing.

The electrodes were submerged to about the same level. If the vessel remained closed after the electrodes had come to equilibrium, the flow of hydrogen could be stopped for thirty minutes or even more without changing the potential. This was a great convenience when working with liquid junctions.

Amalgam Electrodes. Amalgam electrodes have been described by several investigators. Much experimentation was done on the strength of amalgams most suitable for this work. The concentrations of sodium were varied from 0.5 to 0.01 per cent. As the amount of sodium was increased, the amalgam became more negative with respect to the solution and the potential became more stable, but unfortunately a more rapid decomposition of amalgam took place, thus changing the concentration of the solution. In solutions of 0.02 molal or less, approximately 0.01 per cent amalgam was found to be the most suitable. Precautions were taken to have the minimum contact of amalgam with the solution. For example, it was found that after the amalgam was in contact with 0.01 molal sodium hydroxide for about 15 minutes, a devia-

tion of several tenths of a millivolt was sometimes observed, due to concentration changes in the solution. Under proper technique, which required a long time to develop, this deviation became negligible. With stronger solutions higher concentrations of sodium in the amalgam were used. The absence of air is absolutely necessary for the proper functioning of the amalgam electrodes. This was accomplished by passing hydrogen into the solution for about two hours. The hydrogen was purified by passing it over platinized porous plate heated to $200^{\circ}\text{C}.$, and was then bubbled through solution of the same concentration as in the cell.

Cells Without Transference. The entire cell combination is represented in Fig. 1. Sides (1) and (2) were as nearly symmetrical as possible, except for the concentrations of the sodium hydroxide solutions. In all the work the inside of the cells and glass connections was coated with paraffin. The amalgam elec-

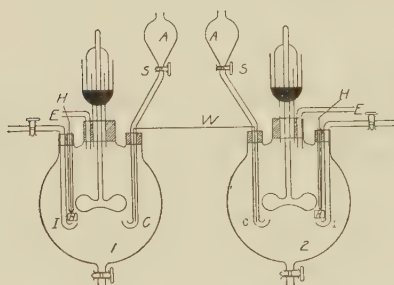


FIG. 1. Cells without transference.

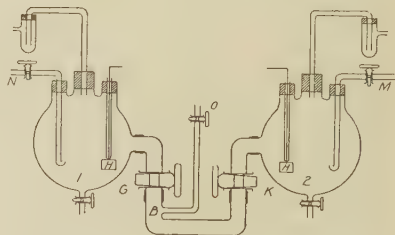


FIG. 2. Cells with transference.

trodes (A) were electrically connected by means of a wire (w). In each of the vessels were three hydrogen electrodes (H), which were checked against one another before each series of measurements. The hydrogen entered the vessel through (I), passed through the solution, and escaped through exit (E), where it bubbled through a small amount of distilled water. After the hydrogen had passed through for about an hour, the electrode came to equilibrium. Another hour was allowed to insure more complete saturation. The leads were connected to the potentiometer and the stirrers started. The stopcocks (S) were opened slightly, so the amalgam could drip from the cups (C). The rate of flow was so regulated that from one to two drops fell per second. Equilib-

rium was not always reached immediately. The key of the potentiometer was pressed down, and if the reading remained constant to 0.1 or 0.2 millivolt for thirty seconds or more it was recorded. The stirring was then immediately stopped, as was the flow of the amalgam. The amalgam which had accumulated in the bottom of the vessel was drawn off as quickly as possible.

When this was done the potentiometer was again balanced against the standard cell, the stirrer started and the process repeated. In this manner at least four readings were taken. The amalgam was in contact with the solution during a minimum of time, which was especially important in dilute solutions, where the effect of a small amount of decomposition was relatively great. Entirely fresh solutions were then used and the whole procedure repeated.

Cells With Transference. The cells used were of the type represented in Fig. 2. Vessels (1) and (2) contained, respectively, the dilute and the concentrated solutions.

In the preliminary runs the dilute sodium hydroxide was colored with a few drops of phenolphthalein solution, so that the boundary could be clearly observed. On making a fresh boundary, the line of demarcation between the two liquids was surprisingly sharp, but the sharpness was soon obliterated by diffusion. When the boundary was renewed it again became sharp. The potentials, however, of the sharp and diffused boundaries were identical, unless the sodium hydroxide concentration was approximately 0.005 molal or less, in which case a sharp boundary had a slightly higher value.

When the apparatus was ready and the solutions were saturated with hydrogen, the stopcocks (G) and (O) were opened and sufficient solution was drawn off at (O) to insure fresh solution to (B). (G) was then closed and (K) opened and solution was similarly drawn from flask (2). The flasks were so adjusted that the height of the solutions was the same in each flask, and the hydrogen electrodes were submerged to about the same depth. The stopcocks (O), (M) and (N) were closed and G and K opened. The potential was immediately read. Again (M) and (N) were opened and the boundary at (B) was reformed in the same way as before, and another reading taken. When such a boundary had

been properly made, further renewals caused no change in potential. In fact, the boundary remained constant for hours, although it was frequently renewed to make sure no further change would take place.

EXPERIMENTAL RESULTS.

The data obtained with both types of cells are recorded in Table II. At least four readings were taken with each pair of solutions; the cells were then cleaned out and refilled with the same pair of solutions and another set of readings taken. The values recorded are the averages of the averaged values. For cells without transference the maximum deviation of the averaged values amounted to 0.2 millivolts. For the cells with transference the maximum deviation of the averages was 0.10 millivolts. Column C_1 gives the concentration of the dilute solution in moles per kilogram of solvent. Column C_2 gives the concentration of the stronger solution. E is the electromotive force in millivolts for the cell without transference and E_t is the electromotive force of the corresponding cell with transference. All measurements were made at $25^\circ \pm 0.01^\circ \text{C}$.

TABLE II.
Summary of Experimental Data.

C_1	C_2	E	E_t
0.01004	0.02578	46.0	9.10
0.01289	0.02578	34.1	6.71
0.02578	0.0644	44.3	8.69
0.02578	0.1288	76.9	14.82
0.01289	0.2574	144.4	27.05
0.2574	0.3517	17.3	3.12
0.3517	0.9738	47.9	8.08
0.9738	1.482	23.0	5.78
1.482	2.825	40.7	6.52

DISCUSSION OF RESULTS.

Activity Coefficients. The activity coefficients were calculated from the equation

$$E = \frac{2RT}{F} \ln \frac{\gamma' c'}{\gamma'' c''}$$

which at 25° reduces to

$$E = 118.3 \log \frac{\gamma' c'}{\gamma'' c''}$$

In order to calculate the activity coefficients at any concentration, some assumption must be made with regard to the activity coefficient at a definite concentration. The assumption commonly made is that at extreme dilution the activity coefficient equals the conductance ratios or ionization. Knobel⁸ assumed the value for 0.001 molal potassium hydroxide to be 0.989; for 0.01 molal it becomes 0.92. Harned⁹ assumed the activity coefficient of 0.01 molal sodium hydroxide to be 0.92. Since the lowest concentration, 0.01004 molal, used in this work is so close to 0.01, the same value, 0.92, for activity coefficient was assumed in this calculation.

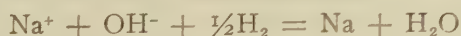
TABLE III.

Summary of Electromotive Force Measurements and Activity Coefficients.

1 C ₁ Mols. per kg. solv.	2 E (Meas.) mv.	3 E (Harned) mv.	4 Act. C ₁	5 Act. Coeff. uncor.	6 Act. Coeff. cor.	7 Act. Coeff. (Harned)	8 Act. Coeff. (L & R)
0.01004	00.0	00.0	0.00924	0.920	0.920	0.920	0.920
0.01289	11.9	11.9	0.01164	0.903	0.903	0.906	0.910
0.02578	46.0	45.5	0.02261	0.877	0.877	0.865	0.877
0.0644	90.3	88.7	0.05356	0.832	0.831	0.808	0.831
0.1288	122.9	121.2	0.1010	0.784	0.783	0.765	
0.2575	156.3	155.0	0.1935	0.752	0.749	0.734	
0.3717	173.6	172.5	0.2710	0.729	0.725	0.717	
0.9738	221.5	220.5	0.6884	0.707	0.695	0.679	
1.482	244.5	244.5	1.077	0.727	0.708	0.706	
2.825	285.2	286.8	2.378	0.842	0.796	0.819	

The results of such calculations are given in Table III, column 5. Column 1 gives the concentrations in gram molecules per 1,000 g. of water. The values in column 2 represent the potentials which would be obtained from concentration double cells having concentrations C₁ on one side and a concentration 0.01004 moles per kg. water on the other.

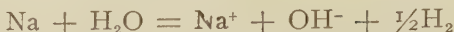
In the halves of the concentration double cells used in this work, the reactions which take place on the passage of one faraday are, on the more concentrated side:



⁸ J. Am. Chem. Soc., **45**, 70 (1923).

⁹ J. Am. Chem. Soc., **47**, 676 (1925).

on the more dilute side :



The net result is the loss of 1 gm. eq. of Na^+ and 1 gm. eq. of OH^- and the gain of one molecule H_2O on the concentrated side, while on the dilute side there is a gain of 1 gm. eq. of Na^+ and 1 gm. eq. of OH^- and a loss of one molecule H_2O . Equating the expressions for osmotic and electrical work

$$EF = \frac{A_{\text{Na}^+} (C_1) A_{\text{OH}^-} (C_1) A_{\text{H}_2\text{O}} (C_2)}{A_{\text{Na}^+} (C_2) A_{\text{OH}^-} (C_2) A_{\text{H}_2\text{O}} (C_1)}$$

or

$$E + 0.591 \log \frac{A_{\text{H}_2\text{O}}^{\text{O}} (C_1)}{A_{\text{H}_2\text{O}} (C_2)} = 0.1183 \log \frac{\gamma_1 C_1}{\gamma_2 C_2}$$

It is evident from this formula, as Harned¹⁰ pointed out, that the measured electromotive forces should be corrected for the difference in activity of the water on the two sides of the cell. Harned made such calculations over a concentration range from 0.0202 M to 3.1 M NaOH. In the present work the corrections were obtained from a plot of Harned's values of electromotive force corrections against concentrations. These corrections are all negative, that is, they are subtracted from the measured values of e. m. f. For the lower concentrations the corrections are negligible, and the correction is less than three millivolts at the highest concentration. The change in activity coefficient, however, resulting from this largest correction is 0.046. The activity coefficients calculated from these corrected e. m. f. values are recorded in column 6.

In the work by Harned referred to above, the electromotive forces of cells of the same general type as used in this work were measured, and over approximately the same concentrated range. We plotted his results against concentrations and then took the e. m. f. values from the curve corresponding to the concentrations used in our work. These e. m. f. values are given in column 3. It is observed that the agreement is complete at the lowest concentration. The difference increases to a maximum of 1.7 mv., then decreases to absolute agreement at next to the highest concentration. Our values are consistently slightly higher except for the

¹⁰ J. Am. Chem. Soc., 47, 676 (1925).

highest concentration. The slight discrepancy between Harned's values and ours is probably due to the different methods employed. Harned made use of the flowing amalgam electrode in a rather quiet solution, the amalgam flowed from a narrow opening; while we used an amalgam electrode rather broad and cup-shaped, in a vigorously stirred solution. The amalgam flowed over the edge of the cup at the rate of about two drops per second. It was observed all through our work that stirring increased the potential slightly, and that the increase was greater the more vigorous the stirring up to a certain limit. This effect was greatest in the dilute solutions. The paddles of the stirrer moved close to the surface of the amalgam.

The activity coefficients obtained from Harned's data, corresponding to the various concentrations used in our work, are recorded in column 7. A comparison of the corresponding values in columns 6 and 7 emphasizes the fact that e. m. f. measurements must be made with extreme accuracy if activity values calculated from them are to have only a small percentage error. This is evident, also, from the equation

$$E = K \ln \gamma_1 C_1 - K \ln \gamma_0 C_0$$

where γ_0 and C_0 represent the activity coefficient and concentration of the reference solution.

$$\text{Then } dE : K \frac{d \gamma_1}{\gamma_1} \text{ or } \frac{d \gamma_1}{\gamma_1} = K' dE = 19.48 dE$$

This shows that the relative change in activity coefficient is about twenty times the change in e. m. f. in volts.

On the basis of the hypothesis of the independent activity of ions in dilute solutions, Lewis and Randall¹¹ calculated the activity coefficients of several ions at various concentrations. From their values of the Na^+ and OH^- ions, we obtained the activity coefficient of sodium hydroxide at some of the concentrations used in our work. They give values for only low concentrations. These values are recorded in column 8. A comparison of the values in columns 8 and 6 shows very close agreement. This is interesting, at least.

¹¹ Thermodynamics, p. 382.

Transport Numbers. The potential of a concentration double cell as used in this work is given by the equation

$$E = \frac{2RT}{F} \ln \frac{a_1}{a_2}$$

The potential of another concentration cell in which the solutions are the same, and in which hydrogen electrodes are used, but having boundary potential, is given by the equation

$$E_t = \frac{2 N_c RT}{F} \ln \frac{a_1}{a_2}$$

From these equations it is evident that the transport number is given by the equation

$$N_c = \frac{E_t}{E}$$

This holds true, however, only under the condition that N_c remains constant between the concentrations used. An accurate expression is

$$N_c = \frac{d E_t}{d E}$$

The value for $\frac{dE}{d \ln a}$ is constant and equal to 0.1183. The value for $\frac{dE_t}{d \ln a}$ at any concentration may be obtained from a curve in which E_t is plotted against $\ln a$. Because of the difficulty of obtaining the slope of such a curve from a graph at any given point, MacInnes¹² has suggested fitting an empirical equation to the data, the form of the equation suggested is

$$E_t = A + B \log a \times 10^3 + C \log^2 a \times 10^3$$

When our data are applied to this equation it becomes

$$E_t = 24.32 + 26.38 \log a \times 10^3 - 1.22 \log^2 a \times 10^3$$

This equation gives the value of E in m. v.

In order to show the accuracy to which this equation represents the data the values for E_t were calculated from it. These values are recorded in column 3 of Table IV. The experimental results are recorded in column 2 and the differences in column 4. The nature of these differences shows that the equation is evidently satisfactory.

¹² MacInnes and Beattie, J. Am. Chem. Soc., **42**, 1117 (1920).

The last equation differentiated and divided by the constant 118.3 gives for the transference number of the cation

$$N_c = 0.2230 - 0.0206 \log a \times 10^3$$

The values calculated by means of this equation are recorded in column 5.

In calculating the transference numbers, the uncorrected values for activities, column 4, Table III, were used. It is necessary to use the uncorrected values in this calculation because, in the derivation of the equation for N_c , it was assumed that $dE/d \ln a$ is a constant, and this is only true if the correction for the

TABLE IV.

Summary of Electromotive Force Values for Cells Having Transference and the Calculated Values for Transference Numbers.

1 C_1 Mols. per kg. solv.	2 E_t Meas'd mv.	3 E_t Calcd. mv.	4 Diff. mv.	5 N_c
0.01004	0.00	0.02	— 0.02	0.203
0.01289	2.39	2.42	— 0.03	0.201
0.02578	9.10	9.17	— 0.07	0.195
0.0644	17.79	17.65	+ 0.14	0.187
0.1288	23.92	23.66	+ 0.26	0.182
0.2575	29.44	29.63	— 0.19	0.176
0.3717	32.56	32.64	— 0.08	0.173
0.9738	40.64	40.72	— 0.08	0.165
1.482	44.42	44.45	— 0.03	0.161
2.825	50.94	50.84	+ 0.10	0.153

difference in activity of the water in the two solutions is not made. Since this is the case, it is necessary to use also the uncorrected values for activity in the calculation of N_c .

If it is assumed that the series of E_t values obtained in this work is accurate, then by this method of calculation the values for N_c are reliable to at least one in the third place. If it is assumed that another experimenter were to repeat the measurements and obtain values for E_t which are different from those here recorded by an amount which is relatively the same as the difference between our values for E_t and Harned's values for E_t , the errors introduced in the values for N_c would be less than two in the third place.

